



The effect of benzotriazole on mass transfer in the corrosion of a copper rotating disk electrode

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Received 17 June 1999; accepted in revised form 4 October 1999

Key words: benzotriazole, copper, corrosion, mass-transfer coefficient, rotating-disk electrode

Abstract

The effect of benzotriazole, BTA, on mass transfer in dissolution-corrosion of the copper rotating disk electrode in 0.02 M Fe(III)–0.5 M H₂SO₄ has been studied by means of atomic absorption spectrometry. The mass transfer coefficient, K , was determined from the slope of $\ln(C_0/C)_{\text{Fe(III)}}$ vs. time plots. In the absence of BTA the corrosion process can be described by the correlation $Sh = KR/D = 4.47Re^{0.5}$. The difference in values between Sh and Sh_{Levich} , and the change in slope in the Arrhenius plot points to mixed control for the cathodic process $\text{Fe}^{3+} + 1e^- \rightarrow \text{Fe}^{2+}$ and charge transfer control for the anodic process, $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$. The average activation energies were 7.7 kJ mol⁻¹ and 19.5 kJ mol⁻¹ at (500–1500) and (2000–3000) rpm, respectively. At low concentration of BTA the inhibiting action of BTA increases with concentration and with rotation speed. For $[\text{BTA}] \geq 5 \times 10^{-3}$ M, the K value, 10⁻⁴ cm s⁻¹, remains constant and is independent of rotation rate. The morphology of the copper rotating disk after corrosion in the absence and presence of BTA was examined using scanning electron microscopy (SEM).

List of symbols

A electrode surface, cm²
 C_0 initial Fe(III) concentration, mM
 C Fe(III) concentration at time t , mM
 C_b bulk concentration, mM
 C_i interfacial concentration, mM
 D diffusion coefficient, cm² s⁻¹
 f rotation rate, rpm
 F Faraday constant, 96487 C mol⁻¹
 IE inhibition efficiency
 i_L limiting current density, $\mu\text{A cm}^{-2}$
 K observed mass transfer coefficient, cm s⁻¹
 K_i observed mass transfer coefficient without inhibitor, cm s⁻¹
 K_w observed mass transfer coefficient with inhibitor, cm s⁻¹

K_m mass transfer coefficient in Levich equation, $(0.62\nu^{-1/6} D^{2/3} \omega^{1/2})$, cm s⁻¹
 K_s rate constant on the surface, cm s⁻¹
 n number of electrons transferred in reaction
 R disk radius, cm
 Re Reynolds number $(\omega R^2/\nu)$
 Sc Schmidt number (ν/D)
 Sh Sherwood number $(KR/D = i_L R/nFC_b D)$
 t time, s
 T temperature, K
 V solution volume, cm³
 ρ solution density, g cm⁻³
 μ viscosity, g s⁻¹ cm⁻¹
 ν kinematic viscosity of solution, cm² s⁻¹
 ω angular velocity, radian s⁻¹

1. Introduction

N-heterocyclic compounds have been widely used as corrosion inhibitors [1]. Among these, benzotriazole, (BTA), is known as one of the best corrosion inhibitors for copper and its alloys in a wide range of environments [2–9]. Previous studies have suggested that BTA reacts with copper and forms a three-dimensional complex layer 50 to 5000 Å thick, resulting in corrosion retardation. Protective films have been characterized as polymeric layers of the [Cu(BTA)] complex, using infrared

[10, 11], X-ray photoelectron [11–13], fluorescence and Raman [5, 14, 15], and Fourier transform infrared [15, 16] spectroscopies. However, most of these studies have been conducted using stationary electrodes immersed in stirred solutions of alkaline or low acidity electrolytes.

Applications of the rotating disk electrode, (RDE), in studies of corrosion of copper and its alloys in different media and inhibitors have been carried out using polarization curves [4, 7, 17–20] and impedance spectroscopy [21] techniques. A mathematical model has been developed to predict the effect of dissolved oxygen

on the corrosion of copper-RDE by acidic cuprous chloride [22]. These works deal mainly with the study of the reaction mechanism and the characterization of the protective film.

The aim of the present work was to study the effect of BTA on the dissolution–corrosion of a copper rotating disk by Fe(III) ions in sulfuric acid by means of atomic absorption spectrometry. The mass transfer coefficient for the dissolution–corrosion of the copper-RDE was obtained from Fe(III) concentration–time data. The potentiodynamic measurements were also made using the copper-RDE. The corrosion process is not completely diffusion controlled. The inhibition efficiencies were determined from the decrease in the mass transfer coefficient, and the morphology of the copper surface examined by scanning electron microscopy (SEM) was also considered.

2. Background

(RDE) is a powerful tool for the study of corrosion. The RDE can be used to distinguish between two kinds of control in the corrosion reaction [17]: (a) diffusional control and (b) other types of control, which will be referred to as *chemical* control. If the chemically controlled reaction rate is at least 5 times greater than the diffusion rate, the corrosion process is considered to be completely controlled by the mass transport of the reacting species and the limiting current density for corrosion is given by the Levich equation [23].

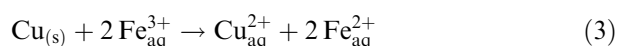
$$i_L = 0.62nFD^{2/3}\nu^{-1/6}\omega^{1/2}C_b \quad (1)$$

The Levich equation can be written in dimensionless form

$$Sh = \frac{i_L}{nFC_bD} = 0.62 Sc^{1/3} Re^{1/2} \quad (2)$$

The dimensionless form is preferred since it facilitates a comparison between other geometries/flow conditions and solutions with different diffusion coefficient values.

The present study was performed using the dissolution–corrosion of a copper disk electrode in an acidified Fe(III) solution, [5, 24–26], following the equation:



The rate of the diffusion-controlled corrosion of the copper electrode in a well-mixed system containing acidified Fe(III) is given by the equation

$$-\frac{dC}{dt} = \frac{KA}{V}(C_b - C_i) \quad (4)$$

For a completely mass transport limited corrosion process, the interfacial Fe(III) concentration, C_i , is negligible compared to the bulk concentration, C_b , and

thus the above equation can be integrated for simple boundary conditions,

$$\ln \frac{C_0}{C} = \frac{KA}{V}t \quad (5)$$

Hence, the K value can be obtained from the slope of the plot of $\ln(C_0/C)$ vs. time. The Sherwood number is evaluated from the experimental values of the mass transfer coefficient by the equation

$$Sh = \frac{KR}{D} \quad (6)$$

3. Experimental details

3.1. Materials

For studies of corrosion in RDE, the specimens were cylindrical copper (99.9% purity) probes 50-mm high and 0.9-cm in diameter covered by a 2-mm polytetrafluoroethylene (PTFE) coating. Prior to each corrosion experiment the working electrode was polished using 200-, 400-, and 600-grade emery papers, rinsed with distilled water and alcohol, and air-dried. A 20-mm long screw was fastened to the upper end of the cylinder to attach it to a Metrohm 628 rotation unit which allowed rotation speeds between 500 and 3000 rpm. After each corrosion run, the disk was repolished and rinsed with distilled water and alcohol.

The initial solution consisted of 0.02 M Fe(III) ions as the oxidant prepared from $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in 0.5 M H_2SO_4 as the supporting electrolyte. The BTA concentration ranged from 0 to 5 mM by the addition of appropriate volumes from a stock solution of 0.1 M BTA (Merck) in 0.5 M H_2SO_4 . Despite the negligible change in the working copper disk, a fresh solution was used in each run to avoid the effect of Cu^{2+} accumulation on the corrosion rate.

All chemicals were of analytical reagent grade. Dissolved oxygen was removed from the test solution by bubbling nitrogen for 10 min. Experiments were carried out at constant temperature with the help of a Selecta Frigiterm S-32 thermostat. The physical properties of the electrolyte at 25 °C were as follows: $\nu = 0.0103 \text{ cm}^2 \text{ s}^{-1}$, $\rho = 1.0442 \text{ g cm}^{-3}$, determined by using a Cannon Fenske viscosimeter and a density bottle, respectively.

3.2. Procedures

3.2.1. Curves I-E

The I-E curves were obtained with a Radiometer VoltalabTM-40 potentiostat/galvanostat. The working electrode was a copper-RDE prepared as described above. The reference electrode was an Ag-AgCl electrode with 3 M potassium chloride and the counter electrode was a 1.2 cm² platinum wire.

3.2.2. Mass transfer coefficient measurement

Before each run, 50 ml of Fe(III)-H₂SO₄ were placed in a Metrohm AG 220 thermostated vessel. Samples of 1 ml of the solution were drawn at 10 min intervals for Cu²⁺ analysis by atomic absorption spectrometry (AAS). AAS was performed with a Perkin-Elmer 100 atomic absorption spectrometer at a 324.7 nm wavelength. For different concentrations of BTA, the mass transfer coefficient K was evaluated from the Fe(III) concentration-time data (Equation 5). The Fe(III) concentration at time t was obtained from the difference between the initial concentration C_0 and the analyzed Cu²⁺ concentration given by Equation (3). The inhibition efficiencies (IE) were calculated from the equation:

$$IE\% = \left(1 - \frac{K_i}{K_w}\right) \times 100 \quad (7)$$

where K_w and K_i are the mass transfer coefficient without and with inhibitor, respectively.

3.2.3. Microscopy

A Jeol-6300 scanning electron microscope was used to study the morphology of the copper surface after corrosion in the presence and absence of BTA.

4. Results and discussion

4.1. Experiments without BTA

Figure 1 shows the polarization curves in the absence of the inhibitor (BTA) at two rotation speeds. Curve (1) corresponds to hydrogen evolution from the supporting electrolyte. It can be seen that hydrogen evolution

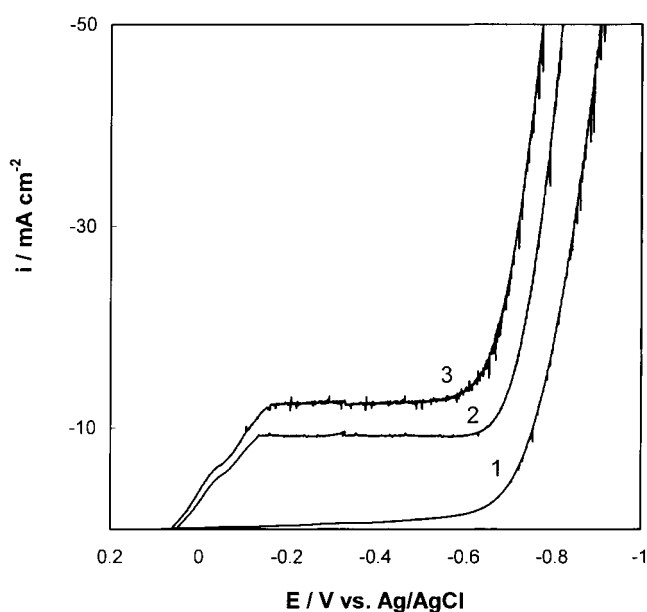


Fig. 1. Current density in Cu-RDE as a function of the electrode potential. (1) Supporting electrolyte 0.5 M H₂SO₄. (2) and (3) 0.02 M Fe(III)-0.5 M H₂SO₄, (2) 1000 rpm, (3) 2000 rpm.

becomes significant at potentials lower than -0.60 V. Curves (2) and (3) represent the reduction of ferric ions from oxygen-free solution at 1000 and 2000 rpm, respectively. Inspection of these curves reveals that a net reduction current for ferric ions is not observed until a potential of 0.05 V is achieved, which corresponds to the corrosion potential for copper in the presence of ferric ions. Similar results were obtained by Bisang [27] using a concentration of 50 ppm ferric ions. The diffusion coefficient of Fe(III) obtained from the limiting currents curves was $5.78 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, in accordance with the estimated value of $5.72 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ obtained from the literature [28] and corrected by means of the mobility product $\mu D/T = \text{constant}$ [29]. In a corrosion process completely controlled by diffusion, the Sherwood number can be calculated by means of the Levich equation, Equation (2). Hence, by substituting the experimental value $Sc = v/D = 1800$ in Equation (2), $Sh_{\text{Levich}} = 7.52Re^{0.5}$ is obtained.

Figure 2 shows a typical plot of $\ln(C_0/C)$ vs. t at different rotation rates in the absence of inhibitor (BTA). The present data fit Equation (5) reasonably. The slope was obtained by regression analysis by the least-squares method. Table 1 shows the values of global mass transfer coefficient, K , at 25 °C for different rotation speeds.

The Sherwood number was calculated from K values, by means of Equation (6). Figure 3 shows the dependence of $\log Sh$ vs. $\log Re$. The data obtained in this work fit the equation $Sh = 4.47Re^{0.5}$. This expression is analogous to the one found in the dissolution-corrosion of a four blade flat turbine of copper in acidified dichromate ($Sh = 17.8Re^{0.5}$) [30].

As $Sh \neq Sh_{\text{Levich}}$, it can be stated that the dissolution-corrosion of copper RDE by acidic ferric sulfate solution is not completely diffusion-controlled. According to

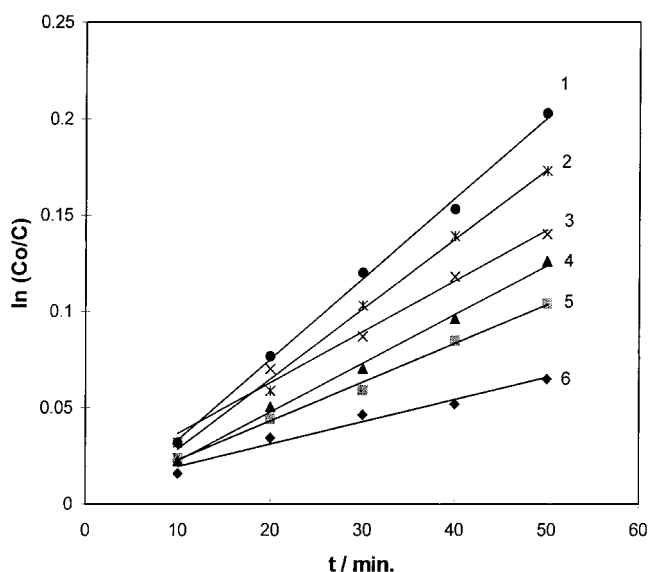
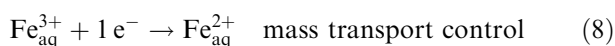


Fig. 2. Plot of $\ln(C_0/C)$ vs. t at different rotation rates for corrosion of Cu-RDE in 0.02 M Fe(III)-0.5 M H₂SO₄ in the absence of BTA. (1) 500, (2) 1000, (3) 1500, (4) 2000, (5) 2500, (6) 3000 rpm.

Table 1. Effect of rotation rate on the mass transfer coefficient for the dissolution–corrosion of the copper disk electrode in 0.02 M Fe(III)–0.5 M H₂SO₄ in the absence of BTA

f/rpm	500	1000	1500	2000	2500	3000
$K \times 10^3/\text{cm s}^{-1}$	1.9	2.7	3.2	3.8	4.3	4.7

Power et al. [31], the corrosion reaction corresponds to the mechanism:



Under the conditions of this work reaction (8) has mixed control so that diffusion and migration across a barrier film on copper during dissolution in H₂SO₄ may contribute to the overall rate of mass transfer. This explains the deviation from the Levich equation. Thus, in a partially mass-transport controlled corrosion process, the observed mass transfer coefficient (K) [32], is given by expression

$$\frac{1}{K} = \frac{1}{K_s} + \frac{1}{K_m} \quad (10)$$

where K_s is the rate constant on the surface of the copper-RDE and K_m is the mass transfer coefficient in the Levich equation,

$$K_m = 0.62 \nu^{-1/6} D^{2/3} \omega^{1/2} \quad (11)$$

From the values of K (Table 1) and the values of K_m , the ratio K_s/K_m can be evaluated, giving a mean value of 1.6. Hence, the rate on the surface is not much higher

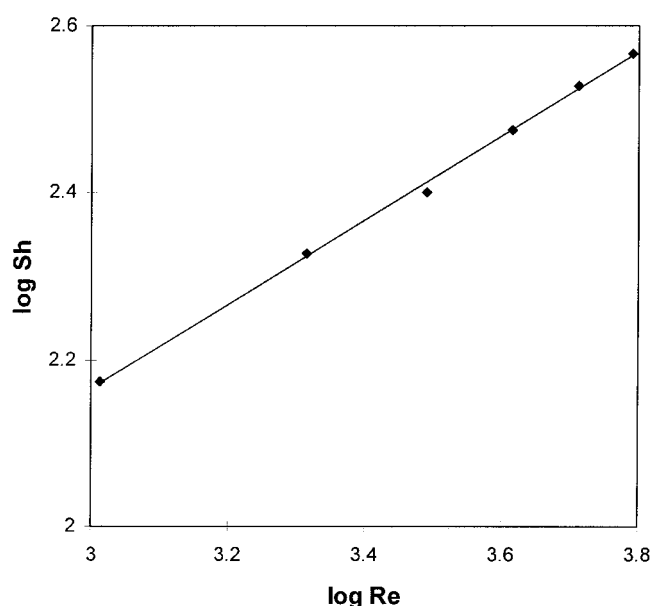


Fig. 3. Variation of Sherwood number vs. Reynolds number for the corrosion of Cu-RDE in 0.02 M Fe(III)–0.5 M H₂SO₄.

Table 2. Effect of BTA on the mass transfer coefficient for the dissolution–corrosion of the copper disk electrode in 0.02 M Fe(III)–0.5 M H₂SO₄

f/rpm BTA/M $\times 10^{-3}$	$K \times 10^3/\text{cm s}^{-1}$					
	500	1000	1500	2000	2500	3000
0	1.9	2.7	3.2	3.8	4.3	4.7
0.2	0.5	0.8	1.1	1.1	1.1	1.1
0.5	0.4	0.5	0.5	0.5	0.6	0.7
1	0.3	0.4	0.4	0.5	0.5	0.5
2	0.2	0.3	0.3	0.3	0.3	0.3
5	0.1	0.1	0.1	0.1	0.1	0.1

than the rate of mass transport and mixed control should take place.

At 35 and 40 °C similar results were obtained, but the slopes in the plot of $\log Sh$ vs. $\log \omega$ were 0.74 and 0.79, respectively. The change in the value of the slope again points to mixed control. The activation energy for copper corrosion for different rotation rates was determined from least squares fitting of the plot of $\ln Sh$ vs. $1/T$ in the interval 25–40 °C. An average value of E_a of 7.7 kJ mol^{−1} at (500–1500) rpm and 19.5 kJ mol^{−1} at (2000–3000) rpm were obtained. These values are in the range of those obtained in copper dissolution under mixed control using ferric chloride [33]. A change of slope in the Arrhenius plot may be due to changes in the reaction mechanism. Thus, a higher activation energy at a higher rotation rate implies mixed control, as the activation energy of a heterogeneous reaction is usually greater than for a diffusion process. A similar behaviour was described in the corrosion rate of copper RDE in air saturated 0.1 M Na₂SO₄ + H₂SO₄ at in the pH range 1 to 3 [17].

4.2. Experiments with BTA

Table 2 shows that the addition of the inhibitor BTA reduces the mass transfer coefficient for copper corrosion depending on the concentration of BTA and of rotation speed. At a given rotation rate, the K values decrease with increase in inhibitor concentration as a result of the adsorption of BTA species and the reduction in the area accesible to Fe(III) ions. At a given concentration of inhibitor, the K values increase with rotation speed. For $[\text{BTA}] \geq 2 \times 10^{-3}$ M, K remains almost constant and does not depend on ω . From the mass transfer coefficients, the inhibition efficiency (IE) at each BTA concentration was calculated according to Equation (7). The results are shown in Figure 4 for two rotation rates. With increasing concentration of BTA, IE increases up to a maximum value close to 95% at 2×10^{-3} M level. These values of IE are higher than those obtained using BTA as the corrosion inhibitor of copper coupons in aerated sulfuric acid ($IE = 60\%$) [15]. The high inhibition efficiency of BTA is thought to result from the formation of complex polymer films on the copper surface [10, 11, 13–16, 34].

Figure 5 shows SEM photographs of the copper surface in the absence and presence of BTA after

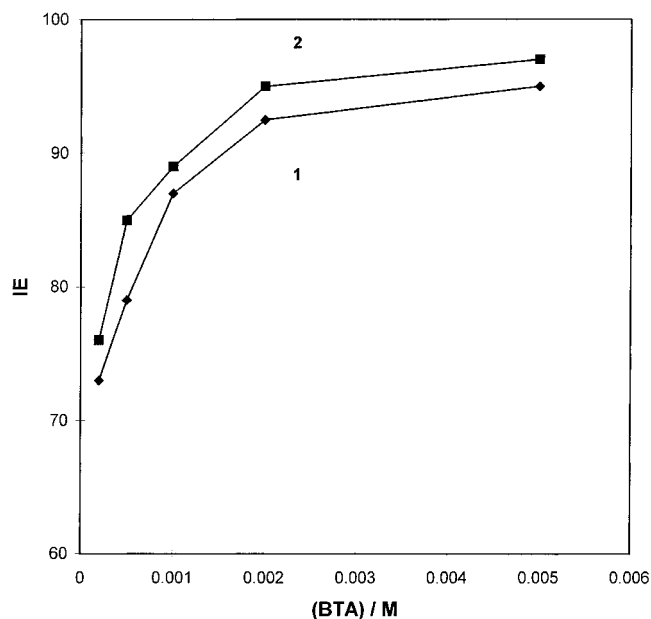


Fig. 4. Variation of Inhibition Efficiency with concentration of BTA. (1) 500, (2) 3000 rpm.

immersing the RDE in the working solution for 45 minutes. When the copper RDE was in a solution without BTA, extensive general corrosion occurred (Figure 5a). In solution with increasing BTA concentrations, the corrosion decreased considerably (Figure 5b–d). The presence of 5×10^{-3} M BTA inhibited corrosion as the surface of the copper immersed in the protected solution appeared identical to that of the blank test.

5. Conclusions

- (i) In the absence of BTA the corrosion process can be described by the correlation $Sh = KR/D = 4.47Re^{0.5}$, indicative of mixed control, where the convective diffusion of Fe(III) ion and the charge transfer reaction have comparable rates.
- (ii) At low concentration the inhibiting action of BTA increases with concentration and rotation rate. For $[BTA] \geq 5 \times 10^{-3}$ M, the K value, $10^{-4} \text{ cm s}^{-1}$, remains constant and is independent of rotation rate.

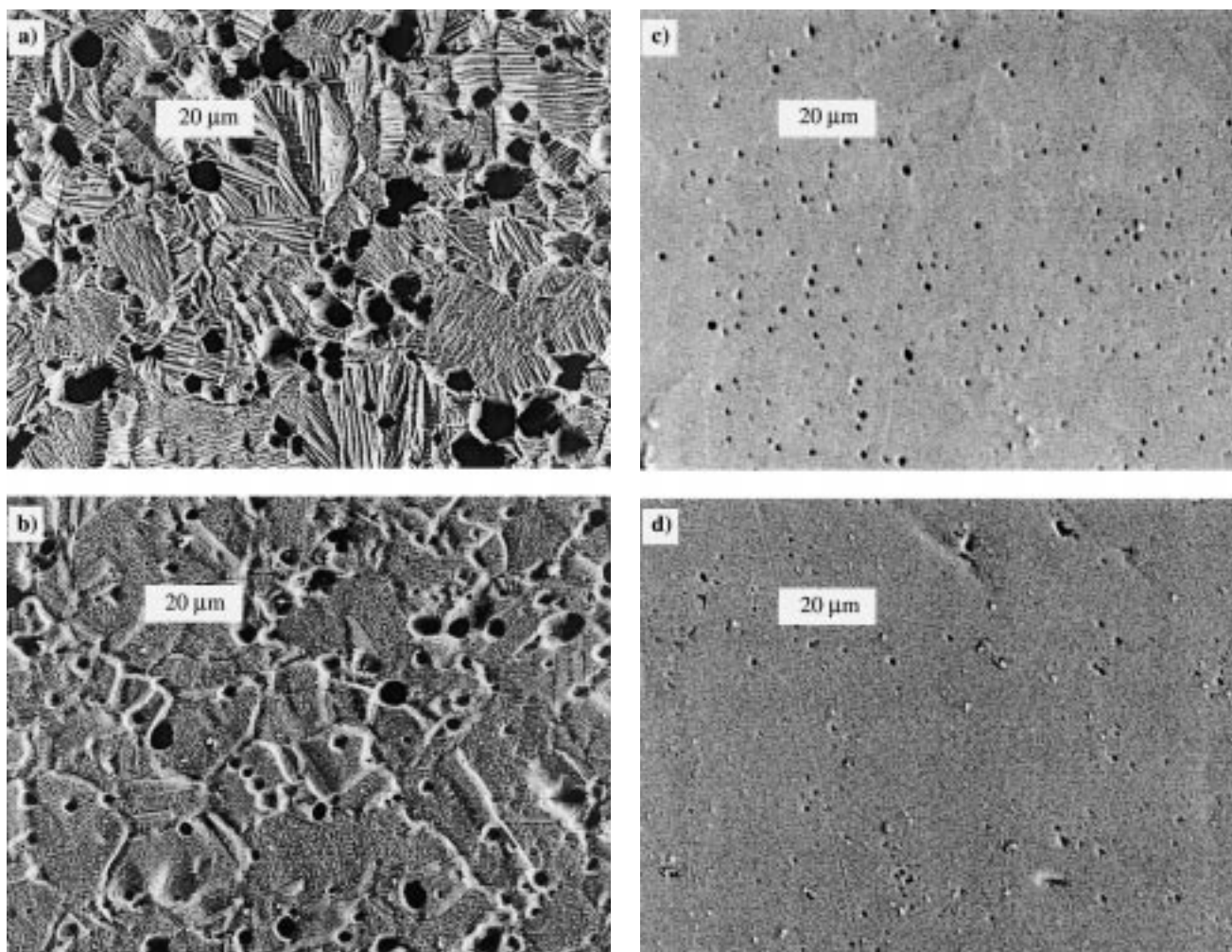


Fig. 5. (a) SEM micrographs of copper RDE after corrosion in 0.02 M Fe(III)–0.5 M H_2SO_4 in absence of BTA. 10 kV, (b) SEM micrographs of copper RDE after corrosion in 0.02 M Fe(III)–0.5 M H_2SO_4 in presence of 2×10^{-4} M BTA 10 kV, (c) SEM micrographs of copper RDE after corrosion in 0.02 M Fe(III)–0.5 M H_2SO_4 in presence of 10^{-3} M BTA 10 kV, (d) SEM micrographs of copper RDE after corrosion in 0.02 M Fe(III)–0.5 M H_2SO_4 in presence of 5×10^{-3} M BTA 10 kV.

Acknowledgement

We thank Maria Asuncion Jaime for her help in translating this paper into English.

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